BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2292—2299 (1973)

The Crystal Structure of Dinicotinic Acid

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(Received January 13, 1973)

The crystal structure of dinicotinic acid has been determined by X-ray diffraction method. Two kinds of twinning crystals were obtained by changing the pH of the aqueous solution by recrystallization. The crystals are monoclinic with the space group of $P2_1/c$ and with cell dimensions of $a=9.702$, $b=11.153$, $c=6.587$ Å, and $\beta=107.8°$. The crystal structure was solved by an inspection of the sharpened Patterson map. The final R value is 5.93% for 1181 observed reflections. The dinicotinic acid molecule takes an intermediate structure between the neutral molecule and the zwitter ion with an approximate C_{2v} symmetry. The bond lengths and angles related by the C_{2v} symmetry are equal within the limits of experimental error for those of the two carboxyl groups. The C(2)–N(1)–C(6) bond angle is 119.8°, which lies between those of protonated and unprotonated species of the pyridine ring. The molecules lie approximately on planes parallel to the (001) plane at $z=1/4$ and 3/4. Each molecules on the same plane is joined through two kinds of hydrogen bonds (O–H···O; 2.594 Å, O···H···N; 2.515 Å), related by two-fold screw axes, with four neighboring molecules. In the O···H···N hydrogen bond, the hydrogen bonding distance and angle are 2.515 Å and 174° and the O–H and N–H distances are 1.23 and 1.29 Å, which are equal within the limits of experimental error. Therefore, it may be considered as an example of the single minimum hydrogen bond of the O–H···N hydrogen-bond type. The existence of two kinds of twins may be interpreted on the basis of the layer structure.

This work is a part of a series of studies on the O–H···N hydrogen bonding by the X-ray crystal structure analyses of several carboxylic acids with a pyridine ring. In their crystal structures studied hitherto, the O–H···N or $^+$N–H···O hydrogen bonds are found to play an important role without exception. Thus, this type of hydrogen bond is formed in nicotinic acid,[1] although the formation of the O–H···O hydrogen bond might also be plausible between carboxyl groups, as has been found in isoelectronic benzoic acid.[2] The same situation has also been revealed in dipicolinic acid,[3] which has a framework similar to that of isophthalic acid.[4] This dipicolinic acid has two bulky carboxyl groups in both α-positions so as to shield the nitrogen atom in a pyridine ring from the hydrogen-bond donor group, but it forms a hydrogen bond between nitrogen and oxygen atoms with the aid of a water molecule. The dinicotinic acid in the present

1) W. B. Wright and G. S. D. King, *Acta Crystallogr.*, **6**, 305 (1953).
2) G. A. Sim, J. M. Robertson, and T. H. Goodin, *ibid.*, **8**, 157 (1955).
3) F. Takusagawa, K. Hirotsu, and A. Shimada, This Bulletin **46**, 2020 (1973).
4) R. Alcala and S. M. Carrera. *Acta Crystallogr.*, **B28**, 1971 (1972).

study is also isoelectronic with isophthalic acid, and it will be of interest to elucidate the effect of the nitrogen atom in a pyridine ring on the hydrogen-bond formation in solids. Furthermore, the melting point of this compound is the highest of the six pyridine-dicarboxylic acids. Therefore, a rather strong hydrogen bond might be expected to exist in this crystal.

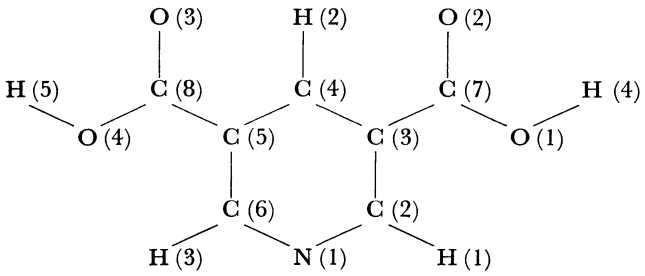
Experimental

Two kinds of crystals were obtained by changing the pH of the aqueous solutions by recrystallization, one in the form of colorless pillars from an aqueous solution and the other in the form of colorless prisms from an aqueous solution containing a few drops of HCl. Weissenberg photographs showed that the crystals recrystallized from an aqueous solution had the a^*b^* twinning plane, and that the other crystals recrystallized from an aqueous acidic solution has the b^*c^* twinning plane. The intensity ratio of the two individuals in the former twin is about 1.0 to 1.0, while that in the latter is 1.0 to 0.15.

The crystals were monoclinic with the space group of $P2_1/c$. The cell dimensions were measured from zero-layer Weissenberg photographs, which were calibrated with superimposed Al powder lines. They are given, along with other crystal data, in Table 1. One of the crystals which had the b^*c^* twinning plane was shaped to a sphere with the average diameter of 0.4 mm. The intensity data were collected for the 0—9 layers around the b axis and the 0—2 layers around the c axis by the use of the multiple-film equi-inclination-integrating Weissenberg technique, using Cu$K\alpha$ radiation. The intensities of the diffraction spots were estimated visually by comparison with an intensity standard. The intensities of the overlapped spots were estimated from $\mathrm{I}\times 0.87$, where I is the intensity of the overlapped spot and where 0.87 is $1.0/(1.0+0.15)$. Of the possible 1555 reflections within the Cu$K\alpha$ sphere, 1289 independent reflections were measured; 108 were too weak to be observed. No absorption correction was applied.

Table 1. Crystal data for dinicotinic acid

Molecular formula	$C_7H_5NO_4$
Molecular weight	167.12
Crystal size	$\sim 0.4\times 0.4\times 0.4$ mm
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell dimensions;	
a	9.702 ± 0.004 Å
b	11.153 ± 0.007
c	6.587 ± 0.004
β	$107.80\pm 0.05°$
V	678.5 ± 0.7 Å^3
Z	4
Density (calculated)	1.636 g/cm^3
Density (observed)	1.63
Radiation	Cu$K\alpha$ ($\lambda=1.5418$ Å)
Linear absorption coefficient	13.65 cm^{-1}
Number of independent reflections	1289
Atom numbering	



Structure Determination and Refinement

The crystal structure was solved by an inspection of the sharpened Patterson map, which was resolved sufficiently enough to give the orientation and the location of molecules in the unit cell. The first postulated structure gave an R value of 42%, which decreased to 13% in three cycles of least-squares refinement with individual isotropic thermal factors. Since the 0 0 2 reflection was seemingly influenced by the strong extinction effect, this reflection was removed from the later refinements.

The coordinates and anisotropic thermal parameters were refined by the block-diagonal least-squares procedure, minimizing the function $\Sigma w(F_o-F_c)^2$, where:

$w=0.5$ for $|F_o|\leqq 0.5$,

$w=1.0$ for $0.5<|F_o|<6.0$ and

$w=6.0/|F_o|$ for $6.0\leqq|F_o|$.

The atomic scattering factors used were those listed in the International Table for X-ray Crystallography for C, N and O atoms and the spherical scattering factors proposed by Stewart, Davidson, and Simpson[5] for the H atom. At the stage of $R=7.9$%, a difference Fourier map was computed, from which five hydrogen atoms were located (Fig. 1). With anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms, the final R value was 5.93%, excluding unobserved reflections. The observed and calculated structure factors are listed in

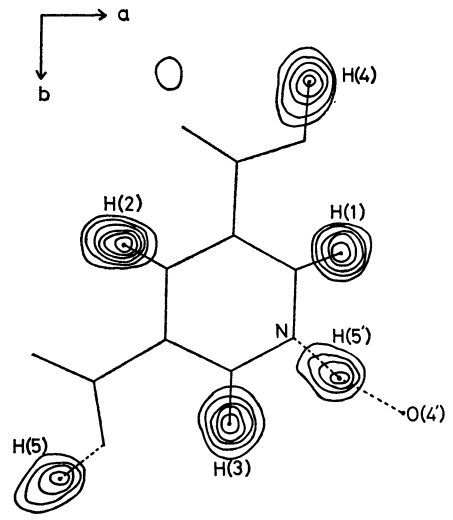


Fig. 1. A composite drawing of the electron density associated with the hydrogen atoms. The contours at intervals of 0.1 e·Å^{-3}, beginning with 0.2 e·Å^{-3} contour.

5) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Table 2. The observed and calculated structure factors

F_o, F_c and DF have been multiplied by 10. The unobserved reflection is indicated by an asterisk. The reflection, for which the $|F_o-F_c|/|F_o|$ is larger than 0.3, is indicated by a plus sign.

H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF
K,L=	0	0		-5	378	-346	-32	2*	0	-6	6	4	46	54	-7	1	56	-56	0	-2	68	65	2	K,L=	4	2	
1	41	-41	0	-4	193	194	-1	3	48	50	-1	5	44	-48	4	2*	0	11	-11	-1	17	18	0	-11+	11	-15	4
2	90	103	-13	-3	236	-229	-6	4	20	-23	2	6	7	9	-1	3+	10	0	9	0	61	-63	2	-10	21	25	-4
3	70	-68	-1	-2	528	500	28	5	67	65	1	7+	6	9	-2	K,L=	2	8		1	65	-64	0	-9	18	20	-1
4	665	-653	-11	-1	447	448	-1	6	11	-12	1	8	53	-53	0	-6*	0	-1	1	2*	0	-2	2	-8	105	-112	7
5	254	232	22	0	23	25	-2	7+	8	-5	-2	9	11	8	2	-5	31	30	1	3	89	-86	-2	-7	23	27	-4
6	109	100	9	1	533	-528	-4	K,L=	1	6		10	45	-40	-5	-4	19	-21	2	4	27	26	0	-6	15	14	0
7	112	111	1	2	316	-314	-1	-10	4	4	0	K,L=	2	3		-3	27	28	0	5	40	40	0	-5+	13	7	6
8	100	-110	10	3	260	273	-13	-9	10	-9	-1	-12+	31	15	15	-2	5	6	-1	6	36	-35	0	-4	209	206	3
9	78	-74	-4	4	123	-131	8	-8	21	-24	2	-11	16	-15	-1	-1	24	-25	0	7	75	72	3	-3	88	97	-8
10	71	68	3	5	309	294	14	-7	11	-10	-1	-10+	7	12	-5	K,L=	3	0		8	35	-33	-2	-2	75	76	-1
11	17	-18	1	6	46	49	-3	-6*	0	-1	1	-9	46	-47	0	1	206	-211	4	K,L=	3	5		-1	115	122	-7
K,L=	0	2		7	27	-29	2	-5	25	-25	0	-8	49	-46	-3	2	167	-180	12	-11	4	3	0	0*	0	-9	9
-12+	13	-8	-4	8	49	56	-7	-4	41	-44	3	-7	123	126	-2	3	316	-289	-26	-10	59	59	0	1	33	37	-4
-11+	4	11	-6	9	86	91	-5	-3	43	45	-1	-6	79	-80	0	4	49	46	2	-9*	0	-1	1	2	16	16	0
-10	82	-91	8	10+	9	-12	3	-2	25	27	-1	-5+	35	-21	-14	5	129	149	-19	-8	44	41	3	3	83	89	-6
-9	87	92	-5	11	14	-15	0	-1	64	62	1	-4	162	-174	11	6	69	-73	3	-7*	0	-3	3	4	117	128	-10
-8	47	61	-13	K,L=	1	2		0	46	48	-2	-3	146	-143	-3	7	172	186	-13	-6	93	95	-1	5	23	-27	3
-7	161	-182	21	-12+	13	-19	5	1*	0	4	-4	-2	56	-56	0	8	121	-123	1	-5*	0	7	-7	6+	9	-14	5
-6	130	-137	6	-11	76	-78	1	2	47	-47	0	-1	101	-103	1	9	35	-35	0	-4	37	-37	0	7	51	-56	4
-5	246	-245	-1	-10+	32	-11	-20	3*	0	-3	3	0	121	118	3	10+	9	-5	-3	-3	8	-10	2	8	82	-79	-3
-4	725	679	45	-9	45	-47	2	4*	0	4	-4	1	330	-322	-8	11	26	-23	-2	-2	68	-63	-4	9	24	25	0
-3	83	-87	4	-8	20	-23	3	5*	0	-5	5	2	17	-19	1	K,L=	3	1		-1	52	-52	0	K,L=	4	3	
-2	119	-109	-9	-7	121	-125	3	K,L=	1	7		3	81	-82	1	-11	13	-10	-2	0	15	15	0	-11	86	78	7
-1	160	-171	11	-6	150	-158	7	-9	51	50	0	4*	0	6	-6	-10	108	113	-4	1	44	-46	1	-10+	9	-4	-5
0	1312	122	-8	-5	65	-69	4	-8+	4	1	3	5	69	60	9	-9	53	56	-3	2	73	-60	-12	-9	148	136	11
1	242	241	1	-4	279	-278	0	-7*	0	-2	2	6	45	39	5	-8	158	162	-3	3*	0	6	-6	-8	146	140	6
2	21	-17	-3	-3	227	220	7	-6	5	7	-1	7	31	28	2	-7	21	20	0	4	15	11	3	-7	70	-71	1
3	122	144	-22	-2	45	46	-1	-5	22	29	-6	8	19	20	0	-6	77	85	-8	5	17	17	0	-6	195	-196	1
4	298	333	-35	-1	245	232	12	-4	33	-34	0	9	31	27	3	-5	147	152	-4	6	14	13	0	-5	116	-110	-5
5	90	-99	8	0	154	156	-2	-3	14	-13	0	K,L=	2	4		-4	4	-4	0	K,L=	3	6		-4	184	185	-1
6	37	-44	6	1	42	40	2	-2	33	-36	2	-12	41	-53	12	-3	178	168	9	-10	22	19	2	-3	18	17	0
7	23	-22	0	2	74	-83	8	-1*	0	-5	5	-11	61	58	2	-2+	18	-25	6	-9	20	-19	-1	-2	397	377	20
8	86	85	0	3	70	-78	7	0	9	-10	0	-10	37	38	0	-1	80	-91	11	-8	55	-50	-4	-1	76	81	-5
9	34	36	-1	4	154	166	-11	1	60	60	0	-9	13	17	-3	0	14	-14	0	-7	117	108	8	0	118	-120	1
10	42	-43	0	5	25	28	-2	2	7	-7	0	-8	11	7	3	1	13	-13	0	-6	26	-27	0	1	150	156	-5
K,L=	0	4		6	145	151	-5	3	11	-13	1	-7	140	-142	1	2	139	-145	6	-5	25	28	-2	2	203	190	12
-12*	0	17	-17	7	25	28	-2	K,L=	1	8		-6	50	-54	3	3	183	-175	-8	-4	33	-37	3	3	17	-17	0
-11*	0	11	-11	8*	0	1	-1	-7*	0	-7	7	-5	56	59	-2	4	15	-17	1	-3	38	-37	0	4+	8	-14	5
-10	78	86	-8	9*	0	9	-9	-6*	0	0	0	-4	68	-64	-3	5	88	-101	12	-2	20	-19	-1	5	105	-106	1
-9	64	-67	2	10*	0	15	-15	-5	14	14	0	-3	127	126	0	6	10	-11	1	-1	12	13	0	6	93	-93	0
-8+	6	-1	-4	K,L=	1	3		-4	13	16	-3	-2	32	31	0	7	23	-29	6	0	28	28	0	7	42	-39	-2
-7	135	140	-5	-12	19	-21	2	-3	12	-15	3	-1	193	-196	3	8	125	-128	3	1	13	15	-2	8	95	90	5
-6	82	90	-8	-11	5	7	-1	-2	10	-10	0	0	107	101	6	9	49	-50	1	2	15	-16	0	9+	8	4	3
-5	101	110	-8	-10	6	7	-1	-1	19	-22	3	1	130	-128	-2	10	62	-62	0	3	37	37	0	K,L=	4	4	
-4	434	-393	-40	-9	116	136	-20	K,L=	2	0		2+	19	2	16	K,L=	3	2		4	11	-11	0	-11+	10	16	-5
-3	82	92	-10	-8	68	71	-2	0	152	164	-12	3+	7	10	-2	-11	42	-34	-7	5	13	-15	1	-10	26	-28	2
-2	38	35	2	-7	40	-41	0	1	513	-535	22	4	22	-22	0	-10+	9	6	3	K,L=	3	7		-9	13	-13	0
-1	97	110	-12	-6	111	109	1	2	35	44	-8	5	32	30	1	-9	42	-42	0	-9	9	12	-2	-8	56	58	-2
1	168	-177	8	-5	231	205	25	3	179	177	1	6+	7	10	-3	-8	125	-139	13	-8+	8	-5	-2	-7	54	-60	6
2	16	-16	0	-4	143	-155	12	4	88	-92	3	7	17	14	3	-7	213	211	1	-7	8	-6	-2	-6	12	-11	-1
3	83	-85	2	-3	57	67	-9	5	49	53	-3	8	25	21	4	-6	61	-67	5	-6	58	-54	-4	-5	10	10	0
4	122	-121	-1	-2	330	-329	-20	6	47	-53	6	K,L=	2	5		-5	140	152	-11	-5	10	10	0	-4	95	-110	15
5	18	22	-4	-1	129	-133	4	7	70	-84	14	-11	22	21	0	-4+	11	-2	-9	-4	18	18	0	-3	23	-29	6
6	17	21	-4	0	34	-40	6	8	74	77	-3	-10*	0	1	-1	-3	242	-244	1	-3	5	6	-1	-2	32	-36	4
7*	0	-8	8	1	288	283	5	9+	18	6	11	-9	57	55	1	-2	162	-155	-7	-2	23	26	-3	-1	64	-64	0
8	39	-38	0	2	78	84	-5	10	65	63	1	-8	25	23	2	-1	122	-112	-9	-1	21	21	0	0+	22	33	-11
K,L=	0	6		3	148	-146	-1	11	24	28	-4	-7	89	-80	-8	0	78	8*	-4	0	15	-15	0	1*	0	0	0
-10	42	-51	9	4	62	61	1	K,L=	2	1		-6	79	73	5	1	174	165	8	1	26	27	-1	2*	0	1	-1
-9	33	32	1	5	161	-156	-5	-12	18	-16	-1	-5	26	28	-1	2	67	76	-9	2	21	16	4	3	42	-44	2
-8	9	-10	0	6*	0	1	-1	-11+	5	0	-5	-4	55	58	-2	3	189	183	6	K,L=	3	8		4	44	-48	4
-7	59	-61	1	7	17	14	2	-10	19	-23	4	-3	21	21	0	4	45	-49	3	-5*	0	-3	3	5	23	23	0
-6	27	-29	1	8	15	-16	1	-9*	0	-1	1	-2	10	-10	0	5	72	-89	16	-4	20	20	0	6	9	10	0
-5	16	-21	4	9	47	-47	0	-8	48	37	10	-1*	0	1	-1	6	53	57	-3	-3	8	7	0	7	40	38	1
-4	172	170	1	K,L=	1	4		-7	136	-140	3	0	23	-23	0	7	130	-128	-2	-2*	0	3	-3	8	31	31	0
-3	39	-46	7	-12+	13	17	-4	-6	27	28	-1	1	146	138	7	8	71	72	-1	K,L=	4	0		K,L=	4	5	
-2*	0	-5	5	-11	58	59	-1	-5	46	-42	-3	2	13	-11	-2	9	24	23	1	0	21	-25	3	-11	78	-71	-6
-1	37	-36	0	-10+	6	2	3	-4	212	207	4	3	13	13	0	10	12	10	1	1	112	-114	1	-10	15	-13	-1
0	236	-228	-8	-9	31	31	0	-3	311	297	13	4+	14	-10	-4	K,L=	3	3		2	57	-65	7	-9	115	-110	-5
1	84	83	0	-8	21	27	-5	-2	156	149	6	5	27	-27	0	-11+	8	-3	-4	3	136	-132	-4	-8	71	-69	-2
2	10	11	-1	-7	66	66	0	-1	416	423	-7	6	22	-20	-2	-10	113	-112	-1	4	219	-220	1	-7	33	32	1
3	30	32	-1	-6	40	44	-3	0	290	-303	12	7*	0	0	0	-9	25	-29	4	5*	0	5	-5	-6	157	146	10
4	29	34	-5	-5	42	44	-1	1	512	568	-55	K,L=	2	6		-8	124	-116	-7	6*	0	3	-3	-5+	21	29	-8
5*	0	-4	4	-4	124	124	0	2	100	109	-8	-10	13	-14	0	-7*	0	1	-1	7	31	34	-2	-4	76	-76	0
K,L=	0	8		-3	120	-118	-2	3	225	239	-13	-9*	0	-8	8	-6	129	-122	-7	8	123	123	0	-3*	0	5	-5
-6*	0	1	-1	-2	43	-45	2	4	72	76	-3	-8	14	15	0	-5	73	-78	4	9	24	-25	1	-2	174	-163	-11
-5*	0	3	-3	-1	151	-151	0	5	86	-85	-1	-7	86	79	6	-4	42	41	0	10+	8	-13	5	-1	8	8	0
-4	53	-62	8	0	114	-107	-6	6	29	-33	3	-6	17	17	0	-3	39	-39	0	11+	5	9	-3	0	32	31	0
-3+	13	18	-5	1	93	-29	-3	7	90	-89	0	-5	52	-50	-2	-2	111	106	5	K,L=	4	1		1	35	-38	3
-2*	0	0	0	2	77	77	0	8*	0	1	-1	-4	36	39	-2	-1	100	97	2	-10+	19	25	-6	2	76	-75	0
K,L=	1	0		3	20	20	0	9	33	-34	0	-3	63	-64	1	0	8	5	2	-9	102	-97	-4	3	20	22	-1
1	97	98	0	4	39	-45	5	10	12	-14	2	-2	19	-16	-3	1	54	57	-3	-8	175	-178	3	4	19	21	-1
2	54	57	-3	5*	0	0	0	11*	0	-4	4	-1	78	73	4	2	145	136	8	-7	100	100	0	5	36	40	-3
3	218	196	21	6	69	-66	-3	K,L=	2	2		0	70	-63	-7	3	64	57	6	-6	201	208	-7	6	39	37	1
4	344	-317	-26	7*	0	4	-4	-12	69	61	7	1	50	50	0	4*	0	0	0	-5	196	202	-6	K,L=	4	6	
5	60	-65	5	8*	0	1	-1	-11	55	-53	-1	2*	0	6	-6	5	12	12	0	-4	217	-204	-12	-10	19	19	0
6	230	-222	-7	K,L=	1	5		-10	65	-62	-3	3	13	10	3	6	18	-19	0	-3	56	-48	-8	-9	7	8	0
7	93	-97	3	-11	10	-8	-2	-9	26	-18	-7	4+	8	5	2	7+	9	18	-8	-2	623	-586	-37	-8	15	-18	2
8	13	-12	0	-10	5	-5	0	-8	57	-54	-2	5	17	-14	-3	8	74	72	1	-1	299	-288	-10	-7	42	45	-3
9	28	-31	3	-9	90	-96	6	-7	156	157	0	K,L=	2	7		9	29	26	3	0	276	243	33	-6*	0	0	0
10	20	-15	-5	-8	23	-25	1	-6	75	80	-4	-9	37	-32	-4	K,L=	3	4		1	331	-330	0	-5	18	-21	2
11	62	-61	0	-7	18	19	-1	-5	57	-55	-2	-8*	0	-5	5	-11	45	39	6	2	439	-443	3	-4	39	43	-3
K,L=	1	1		-6	46	-49	2	-4	99	93	5	-7	43	41	1	-10	18	-17	-1	3	26	-22	-3	-3*	0	-2	2
-12	26	27	-1	-5	76	-78	2	-3	195	-196	0	-6	52	-47	-5	-9	37	34	2	4	69	-74	5	-2	8	9	0
-11*	0	6	-6	-4	76	82	-5	-2	48	-53	4	-5	9	-11	1	-8	99	100	-1	5	183	190	-7	-1	25	25	0
-10*	0	0	0	-3	6	7	-1	-1	415	432	-17	-4*	0	-2	2	-7	174	-175	1	6	157	163	-5	0	19	-23	4
-9	122	-134	11	-2	129	126	3	0	144	-132	-11	-3	10	9	0	-6	43	45	-2	7	84	82	2	1*	0	-2	2
-8	81	-90	9	-1	24	29	-4	1	290	315	-25	-2	18	18	0	-5	81	-87	5	8	149	-146	-3	2*	0	0	0
-7	43	44	-1	0	20	21	0	2	17	-18	1	-1	6	5	0	-4	29	37	-7	9	39	-37	-1	3	17	19	-1
-6	110	-115	4	1	136	-136	0	3	71	-82	10	0*	0	-2	2	-3	118	115	3	10	26	27	-1	4	10	13	-2

TABLE 2. Continued

H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF	H	FO	FC	DF
5*	2	-11	9	K=L=	5	4		9	12	-12	0	-7	12	12	0	5	49	45	4	-4*	6	-9	2	3	79	78	1
K=L=	4	7		-11	93	83	10	10	61	54	7	-6	51	-50	0	6	40	-44	4	-3	39	-38	-1	4	12	-14	1
-8	19	22	-2	-10	27	-26	-1	K=L=	6	2		-5	14	15	0	K=L=	7	5		-2	33	-36	3	5	12	11	0
-7	8	-9	1	-9	56	-53	-3	-11	36	38	-1	-4	11	11	0	-9	23	23	0	-1	36	-35	0	6	34	30	4
-6	87	-84	-2	-8	70	-66	-3	-10	81	-74	-6	-3*	0	-4	4	-8	13	14	0	0	33	-36	2	7*	0	0	0
-5*	0	1	-1	-7	373	-385	11	-9	17	18	-1	-2	35	37	-2	-7	34	38	-3	1	119	-115	-4	K=L=	9	3	
-4	16	14	1	-6	147	152	-4	-8	18	18	0	-1*	0	-4	4	-6	145	-131	-13	2	44	-46	1	-9	73	-61	-11
-3*	0	-3	3	-5	45	48	-3	-7	33	-33	0	0*	0	0	0	-5	19	21	-2	3*	0	0	0	-8	16	-15	0
-2	55	58	-2	-4	80	68	-6	-6	73	70	2	K=L=	7	0		-4	25	-26	0	4	29	31	-2	-7	16	16	0
-1	16	-16	0	-3	150	158	-7	-5	80	-80	0	1	99	-105	5	-3*	6	3	2	5*	9	16	-7	-6	56	-61	4
0*	4	-2	-2	-2	123	-121	-2	-4	20	20	0	2	46	-46	0	-2	82	74	7	6	21	21	0	-5	178	-201	22
1*	0	1	-1	-1	26	-25	-1	-3	197	-210	12	3	35	-35	0	-1*	0	0	0	7*	0	0	0	-4	57	61	-3
2	26	30	-3	0	45	47	-2	-2	82	-81	-1	4	28	-31	3	0	25	-26	1	K=L=	8	4		-3*	8	14	-5
K=L=	4	6		1	105	103	2	-1	94	-102	7	5	100	108	-8	1	43	43	0	-9	38	-39	1	-2	174	177	-3
-5	12	14	-1	2	58	59	0	0	201	-204	2	6	119	-118	-1	2*	0	4	-4	-8	38	36	1	-1	174	172	2
-4*	11	-15	3	3	131	-129	-2	1	29	35	-5	7	25	24	1	3	18	20	-2	-7*	0	1	-1	0	9	10	0
-3	6	6	0	4	29	26	2	2	97	-97	0	8	92	-88	-4	4*	0	3	-3	-6	40	35	4	1	186	-198	12
-2*	0	-1	1	5*	9	3	5	3	109	-116	7	9	67	-68	1	5	8	-11	2	-5	14	-17	3	2	33	-39	5
K=L=	5	0		6*	7	0	-6	4	15	16	-1	10	8	10	-1	K=L=	7	6		-4	71	75	-3	3	35	38	-2
1	211	228	-17	7	148	138	9	5	21	-20	-1	K=L=	7	1		-8	40	-37	-3	-3*	13	-21	7	4*	9	-6	-3
2	356	353	2	K=L=	5	5		6	97	94	2	-10	44	-38	-5	-7	26	29	-2	-2	18	-17	-1	5	154	157	16
3	392	-378	-14	-10	9	7	1	7	41	41	0	-9*	9	12	-3	-6	20	-21	0	-1	44	45	0	6*	3	-8	4
4*	18	27	-9	-9	18	-19	1	8	47	49	-1	-8	49	-42	-6	-5*	10	14	-3	0	189	-173	-15	K=L=	9	4	
5	28	-32	3	-8	64	-65	1	9	13	-13	0	-7	87	88	-1	-4	16	-15	0	1	41	39	1	-9	8	-7	-1
6	34	-32	-1	-7*	17	12	5	K=L=	6	3		-6	182	-182	0	-3*	0	2	-2	2	12	-11	0	-8	21	19	1
7	520	511	8	-6	63	-65	1	-11*	0	0	0	-5	53	-57	3	-2	13	13	0	3	26	30	-3	-7	10	-11	1
8	20	21	-1	-5	66	69	-2	-10	37	-39	2	-4	116	-121	4	-1	18	20	-2	4	21	21	0	-6	16	14	1
9*	18	24	-5	-4	33	34	-1	-9	33	36	-2	-3	102	-97	-5	0	39	41	-2	5	21	22	0	-5	23	-19	-3
10	9	-10	0	-3*	14	-9	-5	-8	57	61	-3	-2	176	167	9	1	21	22	-1	6*	6	-8	2	-4	15	16	0
11	55	-57	1	-2	42	49	-7	-7	51	56	-4	-1	14	16	-2	2	28	-27	0	K=L=	8	5		-3	59	63	-4
K=L=	5	1		-1	32	-33	1	-6	95	-98	2	0	7	-9	2	K=L=	7	7		-9	12	15	-2	-2	11	-14	2
-11	15	11	3	0	15	19	-4	-5*	17	-7	-9	1*	21	14	6	-6	63	68	-5	-8	45	47	-2	-1	73	67	5
-10*	0	-5	5	1	28	30	-1	-4	24	27	-3	2	86	-87	0	-5	26	-27	0	-7	21	-22	0	0	59	-56	-2
-9	15	-17	2	2	6	-4	1	-3	59	-67	8	3	125	120	4	-4*	4	5	-1	-6	52	52	0	1	55	-52	-2
-8	133	-144	10	3*	0	5	-5	-2	172	163	9	4	87	98	-10	-3*	0	-3	3	-5	39	38	0	2	16	13	3
-7*	26	5	20	4	29	-33	3	-1	36	39	-2	5	37	42	-4	-2	28	-26	-2	-4	6	-6	0	3	37	-36	0
-6	96	-96	0	5	9	-9	0	0	19	19	0	6	100	108	-7	-1*	0	4	-4	-3	7	7	0	4	9	9	0
-5	72	82	-10	6*	5	7	-2	1	32	35	-2	7	67	-68	1	K=L=	8	0		-2*	15	-3	-12	5*	5	-8	2
-4	145	152	-6	K=L=	5	6		2	89	83	6	8	55	57	-1	0	372	-362	-10	-1*	16	-6	-10	K=L=	9	5	
-3	126	-122	-3	-9	27	27	0	3	94	-91	-2	9*	8	-12	3	1	83	96	-12	0*	11	19	-8	-8*	0	-1	1
-2	144	135	8	-8	41	40	0	4	27	-27	0	K=L=	7	2		2	71	-67	-3	1	52	59	-6	-7	11	-9	-2
-1	185	-186	1	-7	201	186	15	5	29	-29	0	-10	23	23	0	3*	0	3	-3	3	14	-10	-3	-6	33	31	1
0	24	29	-4	-6	108	-106	-2	6	10	-8	-2	-9	85	-82	-2	4*	95	73	-17	4	14	-14	0	-5	117	104	13
1	173	175	-1	-5	21	-22	1	7	25	26	0	-8	91	-89	-1	5	22	20	1	K=L=	8	6		-4	57	-50	-6
2	83	-82	0	-4	45	-46	0	8	60	59	1	-7	18	17	0	6	41	36	4	-7	8	-6	-2	-3	33	-31	-2
3	104	107	-2	-3	51	-56	5	K=L=	6	4		-6	90	-92	2	7	11	-12	1	-6	15	-16	0	-2	106	-90	-15
4	129	-133	9	-2	32	33	0	-10	79	75	3	-5	93	97	-3	8	41	40	0	-5*	12	16	-3	-1	85	-81	-4
5	35	-41	6	-1	10	13	-2	-9	18	-21	2	-4	28	-36	8	9	37	-39	1	-4	47	-49	1	0*	0	-1	1
6	57	58	-1	0	23	-22	0	-8	29	29	0	-3*	14	-10	-4	K=L=	8	1		-3	10	9	0	1	112	110	2
7*	8	5	3	1	28	-29	1	-7	44	46	-2	-2	34	-30	-4	-10	62	-59	-3	-2*	0	5	-5	2*	0	0	0
8	92	104	-11	2	10	-11	0	-6	36	-29	-7	-1*	14	-18	4	-9	42	-43	1	-1	23	-22	0	3	10	-10	0
9*	4	7	-3	3	50	53	-3	-5	16	16	0	0	62	67	-4	-8	69	66	3	0	82	84	-1	K=L=	9	6	
10*	10	2	8	4	10	-11	0	-4	16	-16	0	1	137	126	10	-7	23	-23	0	1	15	-16	1	-6*	0	-1	1
K=L=	5	2		K=L=	5	7		-3	111	112	0	2	7	6	1	-6	38	37	0	2*	0	-1	1	-5	15	11	4
-11	85	-79	-6	-8	20	22	-2	-2	13	11	1	3	40	43	-2	-5	34	32	1	K=L=	9	0		-4	15	-13	-1
-10*	12	8	4	-7*	0	-2	2	-1	88	84	4	4*	14	-2	-12	-4*	0	1	-1	1	148	-155	6	-3	26	-27	0
-9	53	57	-3	-6	26	32	-6	0	45	50	-5	5	82	-81	0	-3	59	61	-1	2	22	22	0	-2*	3	6	-3
-8	66	66	0	-5	29	-32	3	1	36	-38	1	6	82	88	-5	-2	81	87	-6	3	97	-116	18	-1	29	-26	-3
-7	561	555	6	-4*	5	-7	2	2	44	45	-1	7	34	-34	0	-1	127	122	4	4*	4	8	-4	0	36	31	4
-6	120	-118	-2	-3*	0	-3	3	3	51	52	-1	8	61	59	2	0	53	56	-3	5	5	-4	-1	1	12	15	-2
-5	50	-57	7	-2*	11	-17	5	4	13	-14	0	K=L=	7	3		1	162	160	1	6	36	-41	4	K=L=	10	0	
-4	45	-41	-3	-1	7	7	0	5*	7	-4	-2	-10	34	33	0	2	85	86	0	7*	0	-3	3	0	460	-433	-27
-3	331	-318	-13	0*	3	-4	1	6	63	-55	-8	-9	17	-19	1	3	30	35	-4	8*	8	-11	2	1*	0	1	-1
-2	328	289	38	1	9	-10	0	7	33	-32	-1	-8*	5	-8	-2	4	24	-28	4	9	27	23	4	2*	7	9	-2
-1	91	98	-6	K=L=	6	0		K=L=	6	5		-7	71	-73	2	5*	18	-3	-15	K=L=	9	1		3	7	-5	-1
0	47	-59	12	0	315	321	-6	-10	13	13	0	-6	191	189	1	6*	0	-5	5	-9	90	68	21	4*	63	84	-21
1	203	-215	12	1	34	41	-6	-9	20	-24	4	-5	19	17	1	7	11	-13	1	-8	24	23	0	5	32	-36	4
2	203	-202	-1	2	134	134	0	-8	24	-27	3	-4	76	75	0	8	33	32	0	-7	12	-10	-1	6	60	-67	6
3	253	256	-2	3	203	209	-3	-7	28	-30	1	-3	24	27	-2	9	67	-55	-12	-6	53	59	-6	7	13	-16	3
4	42	-47	4	4	20	-16	-3	-6	85	81	4	-2	163	-146	-16	K=L=	8	2		-5	240	277	-36	8	70	60	10
5*	16	6	9	5	72	74	-2	-5	16	-13	-3	-1	14	-14	0	-10	73	66	7	-4	36	-43	7	1*	7	-12	4
6*	0	-3	3	6	111	-108	-3	-4	24	-23	-1	0	19	23	-4	-9	46	50	-3	-3	41	39	2	2	78	77	1
7	311	-307	-3	7	16	-14	-2	-3	21	25	-3	1	39	-42	3	-8	47	-43	-3	-2	215	-208	-7	3	57	-60	2
8*	15	20	-4	8	55	-58	2	-2	91	-87	-3	2	11	14	-2	-7	10	9	0	-1	272	-259	-13	4	90	87	3
9	10	7	2	9*	0	-2	2	-1*	8	-5	-3	3	74	-70	-3	-6	54	-49	-5	0	10	-8	-2	5*	0	-5	5
K=L=	5	3		10	52	47	4	0*	0	-3	3	4	35	-38	3	-5*	0	6	-6	1	247	269	-22	6	39	42	-3
-11*	11	-7	-4	K=L=	6	1		1*	0	1	-1	5*	0	-3	3	-4	75	-86	11	2	125	132	-6	7	56	51	5
-10*	0	0	0	-10	60	59	1	2	28	-31	3	6	38	-41	2	-3	23	23	0	3	59	-65	5	0	40	40	0
-9	20	23	-3	-9	28	-30	2	3	45	44	0	7	35	36	0	-2	47	47	0	4	15	17	-2	1	36	39	-2
-8	124	124	0	-8	90	-86	-3	4	17	17	0	8	45	-46	0	-1	75	-77	2	5	247	-240	-7	2	22	27	-4
-7*	26	-17	-9	-7	62	-68	5	5	10	8	2	K=L=	7	4		0	284	293	-8	6	23	-22	-1	3	25	18	6
-6	92	97	-5	-6	66	78	-11	K=L=	6	6		-10	34	-31	-3	1	79	-74	-5	7*	0	3	-3	4	42	41	0
-5	95	-98	3	-5	37	41	-4	-9	13	13	0	-9	60	57	3	2	47	45	2	8	11	-11	0	5*	0	8	-8
-4	96	-94	-1	-4*	0	-6	6	-8	38	-39	0	-8	70	64	5	3	28	-31	3	K=L=	9	2		6*	0	-9	9
-3	57	59	-2	-3	116	119	-3	-7	24	-28	4	-7	27	-26	0	4	42	-46	3	-9	23	18	5	1	28	-31	2
-2	100	-106	5	-2	249	-224	-24	-6	18	13	5	-6	45	45	0	5	33	-32	-1	-8	23	-23	0	2	13	14	-1
-1	101	101	0	-1	87	-85	-2	-5	24	26	-1	-5	47	-52	5	6*	11	-8	-3	-7*	4	2	2	3	73	68	4
0	36	-43	6	0	53	-49	-4	-4*	0	4	-4	-4	21	23	-2	7	5	5	0	-6	32	-33	1	4*	0	3	-3
1	86	-86	0	1	81	-83	1	-3	35	-34	0	-3*	12	-1	-11	8	29	-26	-3	-5	16	13	3	5	17	18	0
2	25	27	-1	2	196	-176	-19	-2	10	9	1	-2	6	-4	-1	K=L=	8	3		-4*	0	-7	7	0	4	-5	0
3	40	-41	1	3	126	131	-5	-1	47	-47	0	-1	20	-21	1	-10	55	54	1	-3	92	-108	15	1	16	19	-2
4	72	75	-2	4	22	22	0	0*	0	5	-5	0	69	-69	0	-9*	5	7	-1	-2	23	21	1	2	42	-39	-2
5	16	19	-2	5	47	50	-2	1	15	16	0	1	75	-71	-4	-8	73	-73	0	-1	142	-128	-14				
6	21	-23	1	6	31	37	-6	2	18	-21	2	2	28	28	0	-7	26	25	1	0	58	55	2				
7*	0	-4	4	7	50	-51	1	3	20	-24	3	3	27	-28	1	-6	65	-63	-2	1	124	115	8				
8	50	-53	2	8	86	-84	-2	K=L=	6	7		4	19	23	-4	-5	48	-52	3	2	21	-18	-3				

Table 2. The fractional coordinates and thermal parameters are listed in Table 3.

Results and Discussion

Molecular Structure. The bond lengths and angles are shown with their estimated standard deviations in Fig. 2. Figure 1 shows the difference Fourier map along the *c* axis, in which there is no high peak except for those due to the hydrogen atoms. Figure 3 shows the anisotropic thermal ellipsoids of non-hydrogen atoms and the isotropic thermal ellipsoids of hydrogen atoms.

The dinicotinic acid molecule in the crystal was found by this study to have a structure intermediate between the neutral molecule and the zwitter ion, as

TABLE 3. THE FINAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)

The coordinates of non-hydrogen atoms have been multiplied by 10^4; those of the hydrogen atoms by 10^3. The anisotropic thermal parameters of non-hydrogen atoms are of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$ and have been multiplied by 10^4. For the hydrogen atoms the values listed are isotropic thermal parameters B (Å^2).

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
N (1)	8186 (2)	6534 (2)	2128 (3)	—	O (2)	3892 (2)	4711 (2)	2650 (3)	—
C (2)	6835 (2)	6576 (2)	2266 (4)	—	O (3)	8457 (2)	2272 (2)	2453 (3)	—
C (3)	6120 (2)	5539 (2)	2516 (3)	—	O (4)	10381 (2)	3419 (2)	2819 (4)	—
C (4)	6808 (2)	4453 (2)	2625 (4)	—	H (1)	638 (3)	732 (2)	214 (4)	3.5 (0.6)
C (5)	8204 (2)	4406 (2)	2476 (4)	—	H (2)	630 (3)	367 (2)	284 (4)	3.0 (0.5)
C (6)	8856 (2)	5475 (2)	2235 (4)	—	H (3)	985 (3)	551 (2)	213 (4)	3.9 (0.6)
C (7)	4609 (2)	5591 (2)	2641 (4)	—	H (4)	303 (4)	676 (3)	263 (5)	6.0 (0.8)
C (8)	9039 (2)	3260 (2)	2588 (4)	—	H (5)	1110 (3)	252 (3)	275 (5)	5.6 (0.8)
O (1)	4167 (2)	6697 (2)	2717 (4)	—					

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N (1)	81 (2)	39 (2)	33 (6)	−6 (3)	132 (6)	18 (5)	C (7)	74 (2)	45 (2)	25 (6)	9 (3)	110 (6)	8 (5)
C (2)	85 (2)	39 (2)	30 (7)	1 (3)	128 (7)	1 (6)	C (8)	86 (3)	43 (2)	29 (7)	−6 (3)	117 (7)	−13 (6)
C (3)	77 (2)	40 (2)	23 (6)	1 (3)	103 (6)	3 (5)	O (1)	96 (2)	44 (2)	52 (8)	24 (3)	245 (7)	18 (5)
C (4)	83 (2)	40 (2)	26 (6)	−3 (3)	110 (6)	1 (5)	O (2)	91) 2)	53 (2)	34 (6)	−16 (3)	159 (5)	2 (5)
C (5)	76 (2)	39 (2)	26 (6)	7 (3)	101 (6)	−3 (5)	O (3)	90 (2)	40 (2)	44 (7)	−7 (3)	193 (6)	−9 (5)
C (6)	72 (2)	50 (2)	30 (7)	0 (3)	125 (6)	−3 (6)	O (4)	73 (2)	46 (2)	53 (8)	7 (3)	169 (6)	−39 (5)

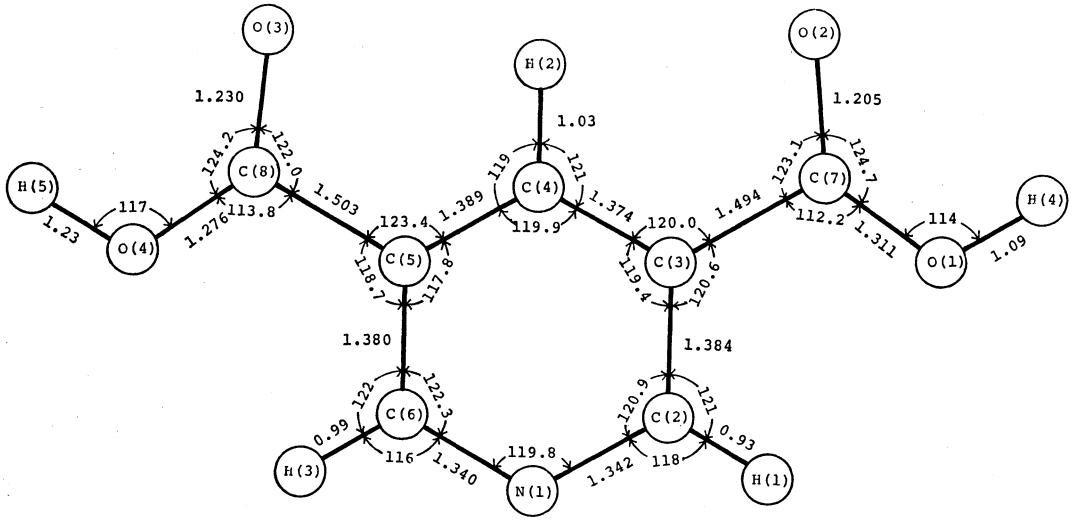
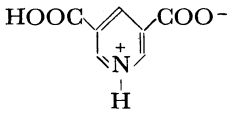


Fig. 2. Dimensions of dinicotinic acid molecule.
The estimated standard deviations are as follows:
X-X=0.003−0.004 Å X-H=0.03−0.04 Å
X-X-X=0.2−0.3° X-X-H=2°
where X and H are non-hydrogen atom and hydrogen atom, respectively.

is shown below;



The existence of the molecule in this form is evident from the position of the hydrogen atom in the difference Fourier map. It is also confirmed by the C(2)–N(1)–C(6) bond angle of 119.8 (2)° and the O(4)–H(5) and H(5)–N(1) bond lengths, which are 1.23(4) and 1.29 (4) Å, respectively (the values in parentheses denote the e.s.d.'s in the last digits).

A dinicotinic acid molecule is approximately planar, with the maximum deviation of 0.229 Å, and its pyridine ring is essentially planar and the maximum deviation of a ring atom from the least-squares plane is 0.002 Å. The equations of the two planes through twelve non-hydrogen atoms of a molecule and six non-hydrogen atoms of the pyridine ring are:

$0.0523X+0.0736Y+0.9951Z=2.3097$ and

$0.0677X+0.0906Y+0.9936Z=2.4951$,

respectively, where X, Y and Z are coordinates in Å referred to an orthogonal set of axes and parallel to the a, b, and c^* axes respectively; this coordinate system

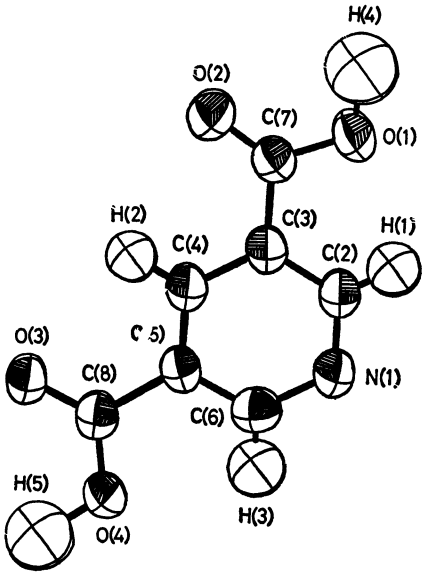


Fig. 3. The anisotropic thermal ellipsoids of non-hydrogen atoms and the isotropic thermal ellipsoids of hydrogen atoms. Ellipsoids are scaled to include 74% probability.

is used throughout this paper. The displacements of all the atoms from the planes are listed in Table 4.

Roughly speaking, the molecule in the crystal has the C_{2v} symmetry, as is shown in Fig. 2. The bond lengths and angles related by the C_{2v} symmetry are equal within the limits of experimental error except for

Table 4.

(1) The distances from the least-squares plane defined by twelve non-hydrogen atoms of a molecule

Atom	Deviation (Å)	Atom	Deviation (Å)
N (1)	0.051	O (2)	0.098
C (2)	0.031	O (3)	0.188
C (3)	0.000	O (4)	−0.229
C (4)	−0.013	H (1)	0.07
C (5)	0.011	H (2)	−0.05
C (6)	0.039	H (3)	0.05
C (7)	−0.005	H (4)	−0.02
C (8)	−0.006	H (5)	−0.15
O (1)	−0.120		

(2) The distances from the least-squares plane defined by the pyridine ring atoms

Atom	Deviation (Å)	Atom	Deviation (Å)
N (1)	0.000	O (2)	0.149
C (2)	0.001	O (3)	0.215
C (3)	0.000	O (4)	−0.251
C (4)	−0.002	H (1)	0.03
C (5)	0.002	H (2)	−0.02
C (6)	−0.002	H (3)	−0.01
C (7)	0.018	H (4)	0.01
C (8)	−0.005	H (5)	−0.17
O (1)	−0.111		

Table 5. The C–N–C bond angles, C–N and N···H bond lengths of several pyridine derivatives

Compound	C–N–C	N–C(1)	N–C(2)	N···H	Reference
Pyridine hydrochloride	128	1.32 Å	1.32 Å	*	a
α-pyridone	125.1	1.401	1.335	*	b
Quinolinic acid	125.1	1.350	1.324	0.89	c
Cinchomeronic acid	122.5	1.349	1.342	1.09	c
Picolinic acid hydrochloride	121	1.39	1.32	*	d
Pyridine hydrogen nitrate	120.4	1.375	1.333	*	e
Dinicotinic acid	119.8	1.345	1.339	1.29	f
Calcium dipicolinate	119.0	1.339	1.326	+	g
Strontium dipicolinate	118.8	1.335	1.335	+	h
Nicotinamide	118.4	1.370	1.336	*	i
Nicotinic acid	117.5	1.343	1.336	*	j
Picolinamide	117.4	1.348	1.335	+	k
Dipicolinic acid	116.8	1.338	1.336	2.17	l
Pyridine	116.7	1.340	1.340	+	m

a) P. C. Reart, *Acta Crystallogr.*, **15**, 427 (1962).
b) B. R. Penfold, *ibid.*, **6**, 591 (1953).
c) F. Takusagawa, K. Hirotsu, and A. Shimada, *ibid.*, **A28**, S15 (1972).
d) P. A. Laurent, *ibid.*, **18**, 799 (1965).
e) A. J. Serewicz, B. K. Robertson, and E. A. Meyers, *J. Phys. Chem.*, **69**, 1915 (1965).
f) This study.
g) G. Strahs and R. E. Dickerson, *Acta Crystallogr.*, **B24**, 571 (1968).
h) K. J. Palmwer, R. Y. Wong, and L. C. Lewis, *ibid.*, **B28**, 233 (1972).
i) W. B. Wright and G. S. D. King, *ibid.*, **7**, 283 (1954).
j) W. B. Wright and G. S. D. King, *ibid.*, **6**, 305 (1953).
k) T. Takano, Y. Sasada, and M. Kakudo, *ibid.*, **21**, 514 (1966).
l) F. Takusagawa, K. Hirotsu, and A. Shimada, This Bulletin **46**, 2020 (1973).
m) B. Bak, L. H. Nygaard, and J. R. Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1958).
* The N···H distance was not determined.
\+ The corresponding N···H bond was not found.

those of the two carboxyl groups. The bond lengths in a pyridine ring are in good agreement with those pyridine itself, but the bond angles are not. The C-(2)–N(1)–C(6) bond angle is 119.8(2),° which lies between the pyridine[6] (116.8°) not protonated at the nitrogen atom and some pyridine derivatives[7–9] (~125°) protonated at the nitrogen atom. The C–N–C bond angles and C–N and N···H bond lengths of several pyridine derivatives are listed in Table 5. The C–N–C bond angle seems to be inversely proportional to the N···H distance, as is shown in Table 5.

Each carboxyl group consists of C–O(H) and C=O groups. The differences between two C–O(H) lengths, C(7)–O(1) and C(8)–O(4), and between two C=O bond lengths, C(7)–O(2) and C(8)–O(3), are 0.035(3) and −0.025(3) Å respectively; these differences are significant in view of their estimated standard deviations. The former difference may be explained by the increase in the double-bond character of the C(8)–O(4) group, which participates in a very short O···H···N hydrogen bond, as will be seen later. On the other hand, the latter difference may be due to the fact that the O(3) atom takes part in the hydrogen bond, while the O(2) atom does not, although there will be a decrease in the double-bond character in the C(8)–O(3) bond corresponding to the increase in this character in the C(8)–O(4) bond. A similar situation is observed also in quinolinic acid[9] and cinchomeronic acid.[9] Therefore, the longer C–O distance in the carbonyl group may be related to the participation of this group in the hydrogen bond. One carboxyl group (C(7)O(1)-O(2)H(4)) twists by 6.7° out of the plane of the pyridine ring, while the other twists by 12.1°.

Molecular Arrangement and Hydrogen-bond System. The crystal structure is shown in Figs. 4 and 5. The distances and angles of hydrogen bonds are listed in Table 6. The molecules lie approximately on the planes parallel to the (0 0 1) plane at $z=1/4$ and 3/4, with a spacing of 3.136 Å. The best plane through the carbon, nitrogen, and oxygen atoms of the 1 and 2 molecules, related to each other by the two-fold screw axis at $z=1/4$, is calculated by the least-squares analysis to be:

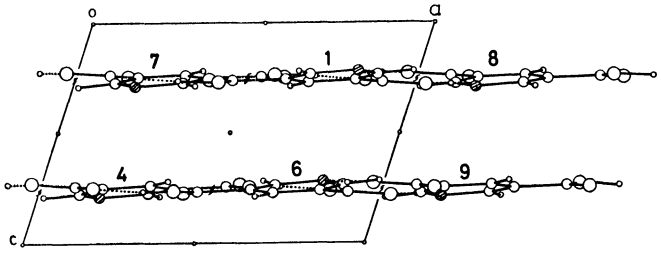


Fig. 4. A view of the crystal structure down the *b* axis. The hydrogen bonds are shown by broken lines. The numbers on pyridine rings correspond to those of the symmetry codes shown in Table 6.

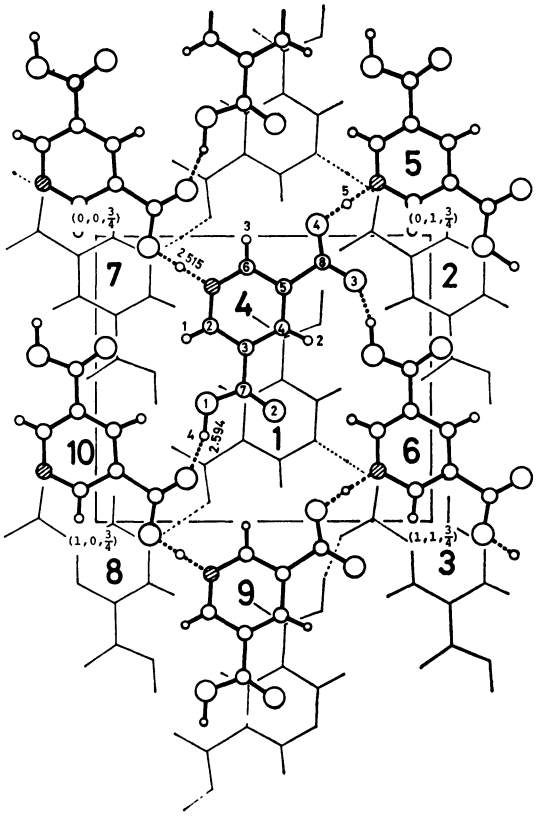


Fig. 5. A view of the crystal structure along the normal to the (001) plane, showing the relative orientation of the molecules in two adjacent layers parallel to the (001) plane. The hydrogen bonds are shown by broken lines. The numbers in pyridine rings correspond to those of the symmetry codes shown in Table 6.

$$0.0279X+0.0240Y+0.9939Z=1.8942.$$

The dihedral angle which it makes with the (0 0 1) plane is 2.1°. Figure 4 shows the crystal structure down the *b* axis. Figure 5 shows a view normal to the (0 0 1) plane and illustrates the relative orientation of the molecules in two neighboring layers. The upper layer of the molecules drawn with heavy lines in this figure involves the molecules on the plane at $z=3/4$.

Each molecule on the same plane is joined through two kinds of hydrogen bonds related by the two-fold screw axes, with four neighboring molecules, and forms a sheet parallel to the (0 0 1) plane. The sheets are related by the center of symmetry and are not linked by the hydrogen bond, but only by the van der Waals forces.

One carbonyl oxygen atom (O(3)) participates in a hydrogen bond (O(3)···H(4)–O(1); 2.594(3) Å), while the other (O(2)) does not. The nitrogen atom in a pyridine ring, however, takes part in a hydrogen bond (N(1)···H(5)···O(4); 2.515(3) Å), as in the crystals of nicotinic acid, dipicolinic acid, quinolinic acid, and cinchomeronic acid. This fact suggests that the O–H···N or $^{+}$N–H···O hydrogen bond is energetically more favored than the O–H···O hydrogen bond in these compounds.

In the O(4)···H(5)···N(1) hydrogen bond, the angle is 174(3)°, which indicates a straight hydrogen bond, and the distance between the O(4) and N(1) atoms is

6) B. Bak, L. H. Nygaard, and J. R. Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1958).
7) P. C. Rerat, *Acta Crystallogr.*, **15**, 427 (1962).
8) B. R. Penfold, *ibid.*, **6**, 591 (1953).
9) F. Takusagawa, K. Hirotsu, and A. Shimada, *ibid.*, **A28**, S15 (1972).

Table 6. Hydrogen bond distances (Å) and angles (degree)

O——H ··· ···X	Symmetry	O···X	e.s.d.	O–H	e.s.d.	H···X	e.s.d.	Angle	e.s.d.
O(1)–H(4)···O(3)	(1, 1, 2)	2.594	0.003	1.09	0.04	1.54	0.04	163	3
O(4)–H(5)···N(1)	(1, 3, 3)	2.515	0.003	1.23	0.04	1.29	0.04	174	3

C——X ··· ···H	Symmetry	Angle	e.s.d.	C——X ··· ···O	Symmetry	Angle	e.s.d.
C(2)–N(1)···H(5)	(1, 1, 3)	119	2	C(2)–N(1)···O(4)	(1, 1, 3)	121.1	0.2
C(6)–N(1)···H(5)	(1, 1, 3)	120	2	C(6)–N(1)···O(4)	(1, 1, 3)	121.1	0.2
C(8)–O(3)···H(4)	(2, 2, 1)	137	1	C(8)–O(3)···O(1)	(2, 2, 1)	130.4	0.2

Symmetry 1=(x, y, z); 2=(1−x, 1/2+y, 1/2−z); 3=(2−x, 1/2+y, 1/2−z); 4=(1−x, 1−y, 1−z); 5=(−1+x, 3/2−y, 1/2+z); 6=(x, 3/2−y, 1/2+z); 7=(1−x, −1/2+y, 1/2−z); 8=(2−x, −1/2+y, 1/2−z); 9=(2−x, 1−y, 1−z); 10=(x, 1/2−y, 1/2+z)

2.515(3) Å, which is very short in the O–H···N type of hydrogen bond. The O(4)···H(5) and N(1)···H(5) bond distances are 1.23(4) and 1.29(4) Å, which are equal within the limits of experimental error. Therefore, this bond may be considered as an example of the single minimum hydrogen bond[16] of the O–H···N type of hydrogen bond. This may also be confirmed by the C(2)–N(1)–C(6) bond angle of 119.8(2)°.

Figure 6 shows the models proposed for two kinds of twins. In the twin(Fig. 6(a)) which has the directions of the *a* and *b* axes in common, the transition may take place across the (0 0 1) plane, since the molecules are arranged in layers closely parallel to this plane and since these layers are stacked together with a spacing of about 3.136 Å. On the other hand, the twin(Fig. 6(b)) which has the directions of the *b* and *c* axis in common may depend on the change in the torsional angle, O(3)–C(8)–O(4)–H(5). Such a twist causes only a little change in the angle and distance of the O(4)···H(5)···N(1) hydrogen bond. Furthermore, no abnormal approach between the intermolecular atoms is found in this twin model because of the layer structure. Therefore, the main reason for the existence of two kinds of twins may be the layer structure in this crystal. It is not easy to explain conclusively the relation between the twinning patterns and the pH of aqueous solutions on recrystallization, since it may be characterized by many factors. However, the formation of two types of twins seems to be related with the amounts of ⟩N, +⟩N–H, —O–H and —O⁻ on the crystal surfaces, which themselves depend on the pH of the aqueaus solution on recrystallization.

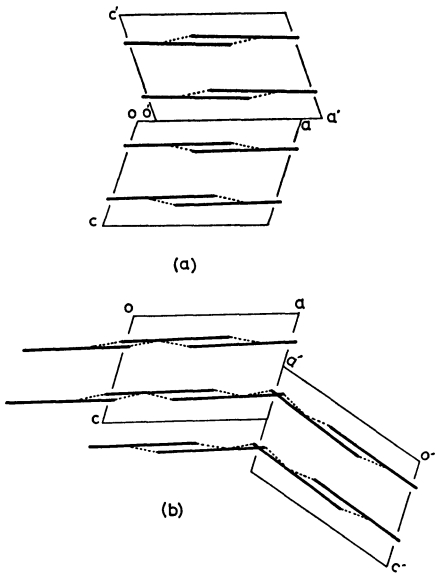


Fig. 6. The model proposed for two kinds of twins. A molecule is shown by a heavy line, and hydrogen bonds are shown by broken lines. (a): This twinning crystal has the directions of *a* and *b* axes in common, and it is obtained from an aqueous acidic solution. (b): This twinning crystal has the directions of *b* and *c* axes in common, and it is obtained from an aqueous solution. In both models, the origins, O and O′, have same value of *y* coordinate, *y*=0.

Computer Programs. All the calculations were performed on a FACOM 270-30 computer at the Computer Center of Osaka City University, using the following programs—RSLC-3 (cell constant),[10] RSSFR-3 (Fourier synthesis),[11] HBLS-IV (block diagonal least-squares refinement),[12] DAPH(bond length, bond angle and least-squares plane),[13] SCALE (film factor, Lp and layer scaling),[14] and TE-I(thermal ellipsoid).[15]

10) T. Sakurai, "The Universal Crystallographic Computing System (I)," edited by T. Sakurai, p. 18, The Crystallographic Society of Japan (1967).
11) T. Sakurai, *ibid.*, p. 45.
12) T. Ashida, *ibid.*, p. 65.
13) T. Ashida, *ibid.*, p. 76.
14) H. Yoshioka, K. Hirotsu, and F. Takusagawa, unpublished work.
15) F. Takusagawa, unpublished work.
16) The "single minimum hydrogen bond" means the hydrogen bond which has the single minimum potential function.